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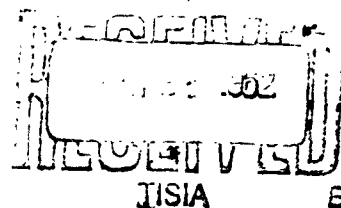
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TEXACO
EXPERIMENT INCORPORATED

RICHMOND 2, VIRGINIA



EXP 223

1 May 1962

COMBUSTION OF ELEMENTAL BORON

Quarterly Summary Report for
February through April 1962

TM-1346

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SUMMARY

Studies of the reaction between elemental boron and fluorine gas have been continued in both the low-pressure microbalance apparatus and in the time-of-flight mass spectrometer. Corrosive failure of the mass-spectrometer apparatus has prevented obtaining the refined data hoped for in the 800 to 1600°K temperature range, although the data available do indicate that at these temperatures BF was the principal species formed on the surface and that the reaction apparently changed to a lower activation energy mechanism when the temperature was raised to about 800°K. Rates obtained in the 525 to 630°K range in the microbalance apparatus gave an activation energy of about 19 kcal/mole, which suggests that the rate-controlling step in this region might be the dissociation of fluorine as it is adsorbed on the surface.

INTRODUCTION

Research on this contract has been concerned with investigating the combustion of elemental boron with various oxidizers to obtain a better understanding of the processes involved. Results of research done on the combustion of boron with oxygen are given in references 1 through 3. The recent research has been on the combustion of boron with chlorine trifluoride (4, 5). This report covers work done during the period of February through April 1962.

QUARTZ MICROBALANCE EXPERIMENTS

The apparatus used for these experiments has been discussed in reference 5b. This was an arrangement for measuring the loss in weight of an externally heated boron rod suspended from a quartz helix in an atmosphere of flowing fluorine at pressures from 1.0 to 0.001 mm Hg. In reference 5c preliminary data are presented in which it was observed that detectable weight changes could be observed at temperatures estimated to be about 600°K. It was noted, however, that in the 1 to 200 μ Hg range the reaction rate seemed to be more dependent on the flow rate than on the pressure, and that on the basis of the rate of weight loss of boron and the flow rate of fluorine, the consumption of fluorine was quantitative.

In order to determine the reaction rate as a function of pressure the equipment was modified to give higher pumping speeds and thus permit higher flow rates at the low pressures required. The geometry of the system and the necessity of an alumina trap in front of the diffusion pump have limited the conductance of the system to the point that the maximum throughput is about 60 liter-microns/sec or about 2×10^8 molecules/sec at 100 μ pressure.

A further modification made was to replace the image furnace, previously used to heat the rod, with a resistance heater wrapped around the quartz tube in the region of the boron rod. This minimized the heating of the quartz helix and caused the boron rod to be heated uniformly to a temperature measured to be about 25° less than the wall temperature in the region of 525 to 630°K. The previously used image furnace caused uneven heating of the rod, and there was the further possibility of a photodissociation of the fluorine, changing the nature of the reaction being studied.

Figure 1 shows the data obtained in a typical run in this apparatus. The step-wise decrease in weight with time has been observed in nearly all of the runs made, and all show the same 3 to 4 min. period. The cause of this behavior is not known but is probably not significant since the maximum deviation of the points from a straight line drawn through the steps (excluding the induction period of 0.5 to 2.0 min.) is less than the instrument (cathetometer) error.

From these data, the rate of consumption of boron was calculated by the following equation:

$$R = 5 \times 10^{-9} S/A$$

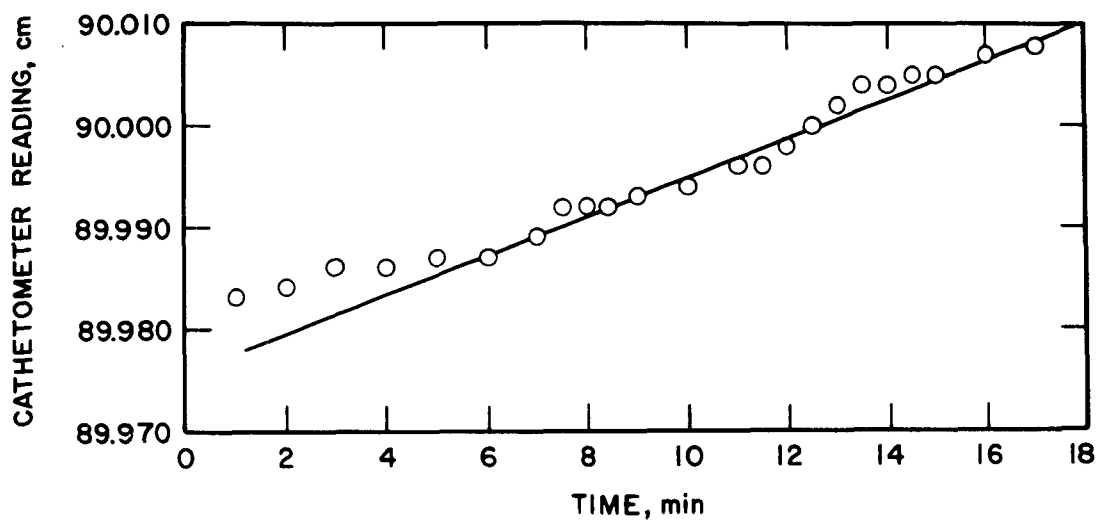


FIGURE 1. DECREASE IN LENGTH OF QUARTZ MICROBALANCE DURING REACTION OF SINGLE-CRYSTAL BORON ROD AT 550 °K WITH FLUORINE GAS

where R is the rate of removal of boron in molecules/cm²-sec, S is the rate of change in the length of the quartz helix in cm/min, A is the apparent surface area of the boron rod, excluding the ends, in cm², and the constant factor includes the Hook's Law constant of 0.0463 ± 0.0003 g/cm of the quartz spring and other necessary conversion factors. The data obtained from experiments on an amorphous boron rod (approximately 1 mm in diameter by 20 mm long) and a single-crystal rod of boron (approximately 2 mm in diameter and 10 mm long) are given in Table 1. An Arrhenius plot of these data is shown in Figure 2. From this plot an activation energy of 19 kcal/mole is obtained.

The qualitative nature of the reaction of fluorine with the single-crystal boron rod is of interest. After repeated runs, the initially smooth cylindrical rod was found to have developed a flat side and several hemispherical craters, two deep cuts, and other surface irregularities. The flat surface could possibly be attributed to the preferential reaction of one crystal face and the other irregularities to preferential reaction along stress lines or at impurity sites. Photomicrographs of the single-crystal rod before and after reaction are shown in Figure 3. Figure 4 shows the rod after reaction with fluorine. After extensive use the amorphous rod assumed a conical shape, and the rate of weight loss became accelerated. This is thought to be due to exposure of the tungsten or tungsten boride core of the rod at the free end and preferential reaction in this area. Although the data obtained were not used in the Arrhenius plot when this distortion became apparent, reaction of the rod was continued until it was only half of its original length. The surface texture of this rod was uniform with the exception of a few craters near the end to which the support wire was welded.

MASS SPECTROMETER EXPERIMENTS

The apparatus used in conjunction with the Bendix time-of-flight mass spectrometer has been previously described (5c). Briefly, the technique is to direct a stream of fluorine gas against the surface of an electrically heated boron rod mounted near the ion source unit of the mass spectrometer so that the species coming off the rod might be detected and measured. Previous experiments showed that BF was present in the mass spectrum in much greater concentration than could be attributed to the electron beam dissociation of BF₃. It was further shown that in the mass-spectrometer experiment the reaction was not detectable until the temperature of the rod was about

TABLE I

CONSUMPTION RATE OF BORON RODS
WITH FLUORINE GAS AT 100 μ

<u>Temperature,</u> <u>°K</u>	<u>Flow Rate,</u> <u>molecules/sec</u>	<u>Consumption Rate,</u> <u>molecules B/cm²-sec</u>
<u>Amorphous Boron Rod</u>		
518	1.26×10^{18}	0.36×10^{17}
533	1.25	0.68
548	1.29	1.3
578	1.39	2.4
613	1.42	8.4
608	1.36	7.9
568	1.34	1.9
538	1.27	1.0
<u>Single-crystal Boron Rod</u>		
628	1.50	6.7
603	1.41	4.0
603	1.43	5.2
588	1.35	2.7
568	1.35	1.5

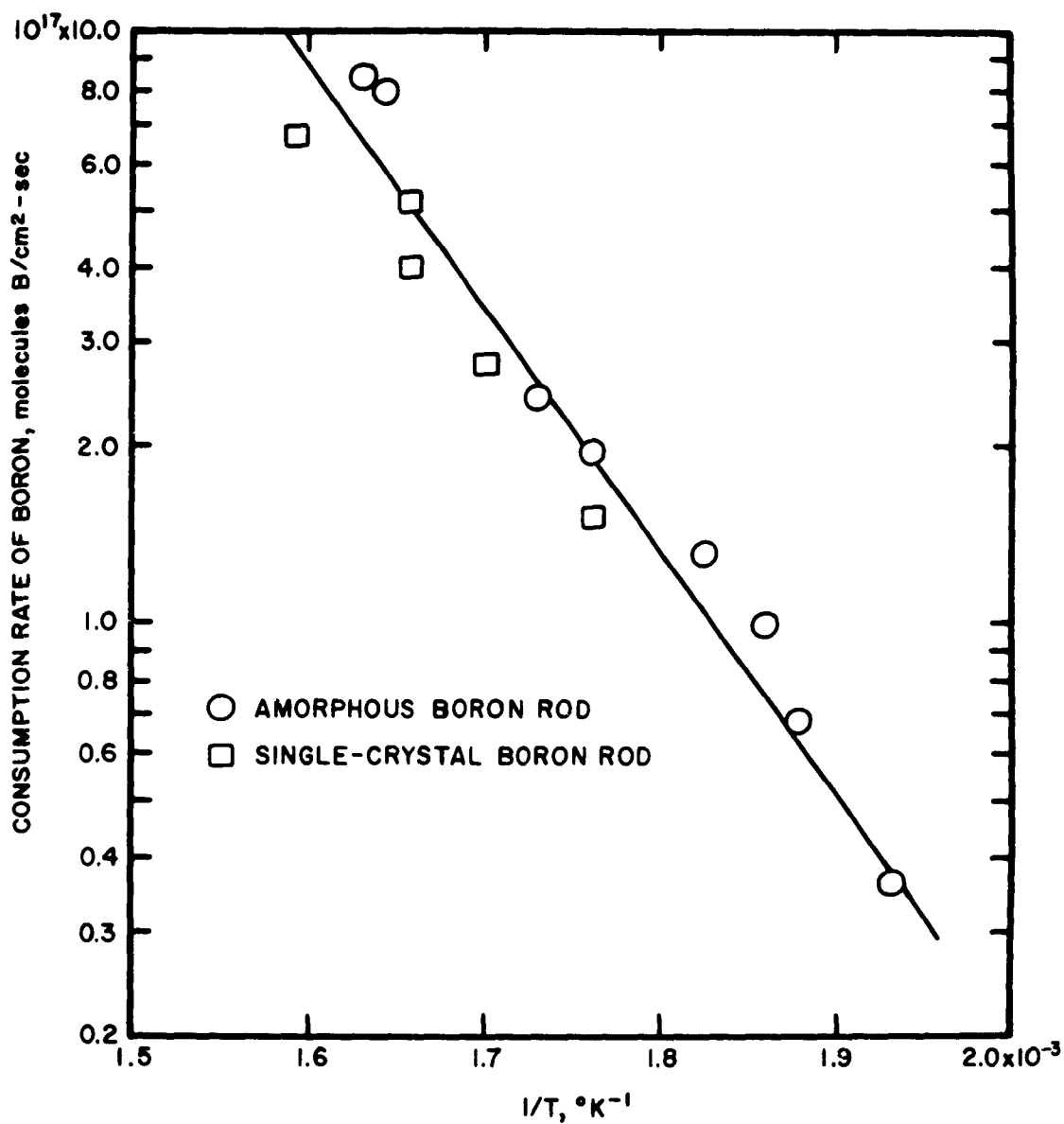


FIGURE 2. OXIDATION RATE VERSUS THE RECIPROCAL OF THE TEMPERATURE FOR AMORPHOUS AND SINGLE-CRYSTAL BORON AT 100μ Hg FLUORINE PRESSURE

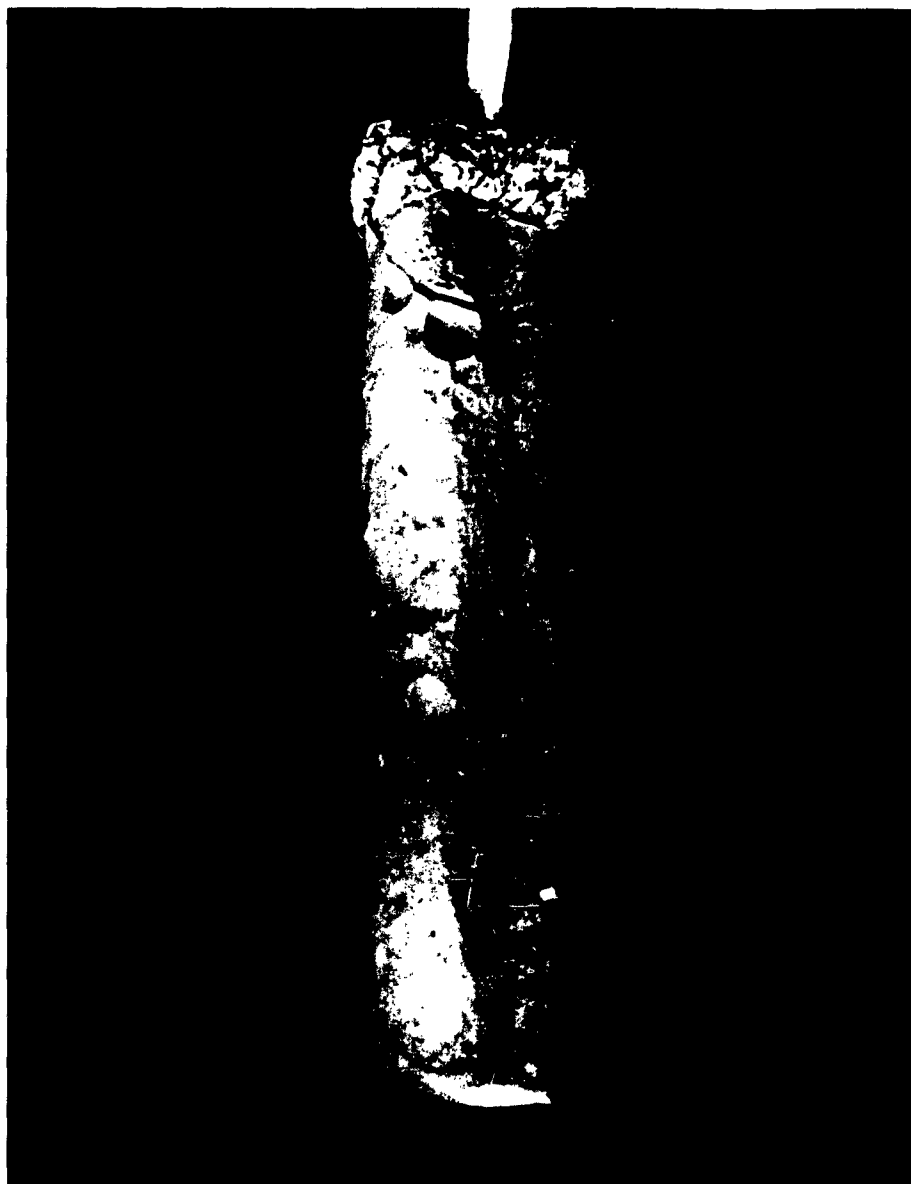


BEFORE REACTION



AFTER REACTION

FIGURE 3. SINGLE-CRYSTAL BORON ROD BEFORE AND AFTER REACTION
WITH FLUORINE GAS



**FIGURE 4. SINGLE-CRYSTAL BORON ROD AFTER REACTION WITH FLUORINE
ETCHED WITH NITRIC ACID TO BRING OUT SURFACE DETAILS**

800°K, at which there was a rather rapid increase in reaction in the 800 to 1100°K range followed by a more gradual increase to the maximum temperature obtainable, about 1650°K.

The data obtained to date are shown in Table II. Runs 1 through 5 are those previously reported; run 6 was obtained during this report period. Some explanation of the quality of the data reported here is in order. From the beginning there has been some uncertainty as to whether the fluorine flow rate remained constant during a run, since if it did not, it would not be possible to extract any temperature dependence from the data. The general observations were that in all runs the intensity of the mass 38 ion peak (F_2^+) decreased with increasing temperature, and the pressure indicated by the ionization gauge in the spectrometer fell gradually during the course of the run, whether the run was made from high temperature to low temperature (the usual manner) or vice versa. These observations have been interpreted as indicating a greater consumption of fluorine at increased temperatures rather than a decrease in flow. The indicated decrease in pressure is consistent with a gradual displacement of air in the gauge tube by fluorine, which would cause an apparent decrease in pressure. The increase in consumption with increasing temperature is not all due to increased reactivity of the boron but is also due to increased reaction on the surrounding surfaces, which are inadequately cooled by the liquid nitrogen trap at the higher temperature of the rod. This statement is substantiated by the fact that the BF_3^+ intensity increases much more than the BF^+ intensity. BF_3 would be expected to form by reaction of fluorine with boron evaporated onto the surrounding cooler surfaces and by reactions of BF gas at the cooler surfaces. It has been shown already that on the hot boron surface BF is the predominant if not the only species formed.

These observations are not inconsistent with a constant fluorine flow during a run, but at the same time it cannot be proved from the data that the flow was constant. In fact, some of the excursions of the data suggest that it was not. To check this point, the fluorine used in run 6 and subsequent runs was labelled with a small amount of helium, whose ion intensity in the mass spectrometer would be dependent only on the flow rate and not on any changes in reaction rate. Unfortunately, run 6 is the only experiment that could be run with this mixture before the apparatus developed extensive unrepairable leaks. It is hoped that new apparatus can be assembled and these experiments continued at a later time. In run 6 the helium ion intensity was found to vary randomly by about 25% from the mean value. The BF^+ intensity, however, increased in a regular manner over twofold; hence by no means all of the change in the BF^+ intensity can be attributed to variations in flow (or perhaps to instability of the instrument electronics).

TABLE II

BF⁺ INTENSITY FOR REACTION OF FLUORINE
WITH HEATED BORON ROD

Run	1	2	3	4	5	6
Mean Pressure, mm Hg	2×10^{-5}	5×10^{-6}	7.5×10^{-7}	3×10^{-6}	2×10^{-6}	2.5×10^{-6}
BF ⁺ Intensity, arbitrary units	1.0 (800°K)	2.8 (800°K)	1.0 (1060°K)	16.6 (1320°K)	0.2 (Ambient)	2.9 (1330°K)
	34.3 (1300°K)	4.5 (1140°K)	2.7 (1140°K)	16.4 (1450°K)	0.7 (1120°K)	3.7 (1430°K)
	34.2 (1470°K)	5.6 (1230°K)	3.4 (1230°K)	10.9 (1630°K)	7.8 (1270°K)	4.1 (1540°K)
	33.3 (1610°K)	6.9 (1420°K)	3.8 (1340°K)		10.8 (1460°K)	6.3 (1670°K)
	46.0 (1680°K)	10.0 (1580°K)	3.9 (1500°K)		9.7 (1630°K)	
			3.4 (1640°K)			

As crude as these data are, it is striking that there is a change in the slope of the rate-temperature curve in the vicinity of 800°K. In this vicinity the apparent activation energy for the reaction drops to 10 kcal/mole or less from a value of 19 kcal/mole obtained in the lower-temperature microbalance experiments. A brief discussion of possible explanations for this behavior is given in the next section.

DISCUSSION

The reaction between fluorine and boron is to form BF formally similar to the reaction between oxygen and carbon to form CO. In addition to the systems BF and CO being isoelectronic, both reactions result in the formation of volatile reaction products. It might be useful, therefore, to consider the oxidation of graphite as a model for the fluorination of boron. The kinetics of the oxidation of graphite have been reviewed by Binford (6). Unfortunately, even the oxidation of graphite is not well understood because of such factors as variations in the surface of the graphite and its crystalline structure. There are, however, some observations that are relevant to the boron-fluorine situation.

It has been observed that at normal pressures the oxidation of graphite is diffusion-limited at temperatures over 700°C. The diffusion limitation of the boron-fluorine reaction has been reported in work on this project (5a), and the diffusion limitation is operative at much lower temperatures than in the graphite case. It is, of course, expected in any fast-reaction situation that the transport of the reactants to the reaction site can become rate-limiting.

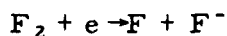
It is generally agreed that at temperatures over 1000°K the primary reaction in the graphite-oxygen reaction is the formation of carbon monoxide. This parallels the observation that BF is the primary product in the high-temperature fluorination of boron. In the 500 to 1000°C range it is reported that both CO and CO₂ are formed in the graphite oxidation reaction.

In the 1000 to 1200°C range the activation energy for the graphite-oxygen reaction is between 20 and 30 kcal/mole, the rate is first-order with respect to oxygen, and adsorption is believed to be the rate-limiting step. The pressure-dependence in the boron-fluorine reaction has not yet been established; however, the activation energy that has been determined (19 kcal/mole) is appropriate for an adsorption mechanism or more probably adsorption with

dissociation of the fluorine, since the energy of chemisorption on metals is quite small (boron can be considered a metal at 500°K), and the energy formation of a fluorine atom is thus the major part of the activation energy.

In the 1200 to 1500°C range the graphite reaction is first-order with respect to oxygen, but recrystallization of graphite gives rise to hysteresis effects, and the rate is found to go through a maximum. Between 1500 and 2000° the reaction is probably first-order but may be zero-order, and observations have been complicated by diffusion effects, thermionic electron emission, and recrystallization.

In the case of boron, it is extremely doubtful that any reversible crystal changes occur in the 800 to 1000°K region to account for the change in rate observed here. There are, however, some possible explanations for this phenomenon. If, for example, the accommodation coefficient approached unity at this temperature (every molecule that hit the surface stuck and reacted), then there could be no further temperature dependence as long as the transport of reactants to the surface and products from the surface are not limiting (which would be the case in the high-vacuum system). Another possibility is that at this temperature an appreciable electron density can build up on the surface of the boron because of thermionic electron emission. It is possible that the presence of these electrons facilitates the dissociation of the F_2 molecule by the following process:



It has been reported that F^- is formed from F_2 by zero-energy electrons (7), and it is conceivable that the gross reaction could be catalyzed by an appreciable number of such electron-transfer processes.

It is hoped that these possibilities can be more extensively explored and discussed in a more quantitative manner in the next report.

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